

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
21 December 2000 (21.12.2000)

PCT

(10) International Publication Number  
**WO 00/77078 A1**

(51) International Patent Classification<sup>7</sup>: C08J 3/00, C08L 77/00, 67/00, 69/00, 59/00

(74) Agent: VAN BORM, Werner, August, Hendrik, Maria;  
DSM Patents & Trademarks, P.O. Box 9, NL-6160 MA  
Geleen (NL).

(21) International Application Number: PCT/NL00/00352

(22) International Filing Date: 23 May 2000 (23.05.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
1012324 14 June 1999 (14.06.1999) NL

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(71) Applicant (*for all designated States except US*): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): BRULS, Wilhel-  
mus, Gerardus, Marie [NL/NL]; Graafwolterhoenstraat  
32, NL-6243 BE Meerssen (NL). REPIN, Johannes,  
Fredericus [NL/NL]; Klingbenden 177, NL-6441 KX  
Brunssum (NL). DE KROON, Jan [NL/NL]; In de  
Neerakker 1A, NL-6093 JH Heythuysen (NL).

Published:

— With international search report.

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: PROCESS FOR THE PREPARATION OF AN IMPACT-RESISTANT POLYMER COMPOSITION

(57) Abstract: The invention relates to a process for the preparation of an impact-resistant polymer composition comprising 0.5-75 parts by weight of a rubber composition (per 100 parts by weight of matrix polymer) by a) melt mixing of matrix polymer A with a composition comprising the rubber composition dispersed in a matrix polymer B, with B optionally being A, and b) the dispersion of said rubber composition in matrix polymer B has been obtained by melt mixing of matrix polymer B with a rubber composition containing at least one functionalized rubber and at least one non-functionalized rubber. The composition according to the process of the invention exhibits an improved impact resistance at less to no creep and is suitable inter alia for use in plugs, as a heat bridge in aluminium windows and profiles and in hammer heads.

WO 00/77078 A1

PROCESS FOR THE PREPARATION OF AN IMPACT-RESISTANT

5

POLYMER COMPOSITION

The invention relates to a process for the preparation of an impact-resistant polymer composition containing 0.5-75 parts by weight of a rubber composition (per 100 parts by weight of the matrix polymer).

Such compositions are known from, inter alia, US-A-4,174,358 and this patent publication discloses various processes for the preparation of these compositions. These processes all essentially comprise a rubber functionalization step followed by incorporation of the functionalized rubber in the desired concentration into the matrix polymer.

20 These state-of-the-art polymer compositions in general exhibit a good impact resistance, which is determined, inter alia, to an important degree by the rubber content of the composition. However, the presence of the rubber composition causes the stiffness to decrease and the creep to increase.

For applications in which no or only minimal creep is allowed while a good impact resistance is required, for instance in plastic hammer heads, it is therefore necessary to have a polymer composition that possesses this combination of conflicting properties. Another application in which this combination of properties is required is that of plastic profiles that serve as heat bridge in metal window and door profiles and screw plugs, where

toughness is required for assembly purposes while no creep may occur when the materials are subsequently subjected to a permanent load. Compositions obtained by the state-of-the-art process, however, cannot fully  
5 meet this requirement.

The aim of the invention therefore is a process for the preparation of an impact-resistant polymer composition that has an excellent impact resistance at no or only minimal creep.

10 This aim is achieved by melt mixing of a matrix polymer A with a composition comprising a dispersed rubber composition in a matrix polymer B, the dispersed rubber composition in matrix polymer B having been obtained by melt mixing of matrix polymer B with a  
15 rubber composition that contains at least one non-functionalized rubber and one functionalized rubber, in such amounts that the desired rubber concentration in the impact-resistant polymer composition is reached.

Also part of the invention are the  
20 composition obtainable by the process according to the invention and the products obtained from the composition according to the invention as well as the (granule) mixture of matrix polymer A and the dispersed rubber composition in matrix polymer B as needed for  
25 the process of the invention.

Matrix polymer A can in principle be chosen freely, but the process according to the invention offers advantages if polymer A is chosen from the group consisting of polyamides, polyesters, polyacetals and  
30 polycarbonates. The invention is effective in particular if polymer A is a polyamide or a polyester.

For matrix polymer B in principle any

polymer can be chosen that can suitably be mixed with polymer A and in which the rubber composition can suitably be dispersed. Preferably, polymer B is chosen from the group consisting of polyamides, polyesters, 5 polyacetals and polycarbonates. Even more preferably, polymers A and B are of the same type of polymer, for instance A and B are both polyamides, for instance an aliphatic and a semi-aromatic polyamide. Most preferably, A and B are identical.

10           The rubber composition dispersed in polymer B comprises at least one non-functionalized rubber and at least one functionalized rubber. Rubber is here understood to mean a polymeric compound with a glass transition temperature lower than 0°C, preferably lower 15 than -20°C, most preferably lower than -40°C.

A rubber is called functionalized when it contains groups that can react with matrix polymer B and/or A.

Examples of polymers covered by the 20 definition of rubber are copolymers of ethylene and  $\alpha$ -olefins, for instance ethylene-propylene rubbers. Very suitable for use in the process according to the invention are the so-called plastomers based on ethylene and C4-C12 olefins, for instance octene, and 25 produced using a metallocene catalyst.

Other rubbers that can suitably be used in the process according to the invention are styrene-butadiene based block copolymers.

Functional groups can be introduced into 30 the rubber in many ways. A great many preparation methods and examples of these functionalized rubbers are described, for instance, in the above-mentioned US

patent publication US-A-4,174,358. Several of these functionalized rubbers are commercially available under different names. Very suitable are rubbers that are chemically modified by reaction with maleic anhydride or by graft polymerization of the rubber with an unsaturated dicarboxylic anhydride or an unsaturated dicarboxylic acid or an ester thereof, for instance maleic anhydride, itaconic acid and itaconic anhydride, fumaric acid and maleic acid or a glycidyl acrylate, for instance glycidyl methacrylate, and vinyl alkoxysilane. The functional groups are highly reactive relative to, inter alia, amino end groups in polyamides, hydroxyl end groups in polyesters and acid end groups in both polyamides and polyesters.

The content of compounds supplying functional groups in the functionalized rubber may vary within wide limits, for instance between 0.01 and 5 wt.%. The best results are generally achieved with a content between 0.3 and 3 wt.%.

The weight ratio of non-functionalized to functionalized rubber may vary within wide limits and is determined in part by the functional groups content of the rubber and the available reactive groups in the matrix polymer. One skilled in the art can determine this by means of simple experiments. In general, this ratio will be between 10 and 0.1, preferably between 5 and 0.1.

The rubber composition content of the composition with matrix polymer B may vary within wide limits, for instance between 20 and 70 wt.%, calculated on the total weight of rubber composition + polymer B, preferably the rubber composition content is chosen as

high as possible, for instance higher than 30 wt.%, more preferably higher than 40 wt.%. Very good results are achieved with contents of at least 50 wt.% or higher.

5           The non-functionalized rubber and the rubber that is functionalized may be identical or different. Combinations are for instance possible of an ethylene- $\alpha$ -olefin copolymer and the same ethylene- $\alpha$ -olefin copolymer modified with, for instance, maleic  
10 anhydride. The same ethylene- $\alpha$ -olefin copolymer may also be combined with, for instance, an acid-modified styrene-butadiene tri-block copolymer.

          Particularly good results are achieved with the process according to the invention when the rubber  
15 composition in matrix polymer B is present in finely dispersed particles. Preferably, the dispersed particles of the rubber composition are then built up of a core of non-functionalized rubber and a shell of functionalized rubber.

20           The composition of matrix polymer B with the rubber composition can be obtained by melt mixing of the constituent components. In doing so, use is preferably made of high shear forces and the conditions are chosen so that the viscosity in the melt of the  
25 rubber phase is higher than that of the polymer matrix. During the melt mixing process crosslinking of the rubber phase may optionally take place. However, a non-crosslinked rubber is preferred. Non-crosslinked rubber is here understood to be a rubber that is substantially  
30 not crosslinked. In practice, however, some degree of crosslinking can hardly be avoided during melt mixing at the high temperatures then prevailing. The resulting

gel content will be lower than 50 wt.%, preferably lower than 30 wt.%, even more preferably lower than 10 wt.%. The gel content is here defined as the rubber fraction that is insoluble in the solvent that is suitable for the rubber in question. For ethylene-propylene copolymer rubbers, for instance, this solvent is xylene. When reference is made to crosslinking of the rubber composition, this is understood to mean the melt mixing process carried out in the presence of a vulcanization agent, for instance a peroxide.

Optionally, the rubber composition can first be crosslinked during incorporation of the composition into matrix polymer A. This process has the advantage that it can be performed under milder and better controllable conditions, so that less damage is done to the matrix polymer, while the process also has the advantage that mechanical properties can be adapted from case to case on the basis of similar compositions.

For mixing in the melt phase the customary techniques and equipment can be employed. Particularly suitable for production of the composition in polymer matrix B is, for instance, a co-rotating twin-screw extruder, while for mixing in of the composition into matrix polymer A in many cases a single-screw extruder, which may be directly prearranged in the injection moulding process, may suffice. Preferably, the mixing operations in the melt are carried out under an inert gas atmosphere.

During melt mixing optionally the customary additives and auxiliary materials for the polymer compositions can be added, for instance stabilizers, colourants, processing aids, for instance release

agents, flame-retardant additives and fillers or reinforcing (fibre) materials. Preferably, the additives and auxiliary materials are introduced into the melt only after the rubber composition has been  
5 dispersed in the matrix polymer.

Most preferably, the auxiliary materials and additives are added to the melt of polymer A, optionally simultaneously with the mixing in of the composition of polymer matrix B or separate therefrom.

10 The invention will now be elucidated on the basis of the following examples and comparative examples.

Materials:

15	AKULON <sup>®</sup> F235C	polyamide-6, rel. visc. 2.3, from DSM
	AKULON <sup>®</sup> 223 TP4	blend of polyamide 6 and Excellor <sup>®</sup> (80:20) from DSM, Netherlands
	AKULON <sup>®</sup> K 120	Polyamide-6, rel. visc. 2.2, from DSM
20	EXXELOR <sup>®</sup>	ethylene-propylene rubber modified with 0.7 wt.% maleic anhydride from Exxon, USA
	KRATON <sup>®</sup> FG 1901X	styrene-butadiene block copolymer, modified with 2 wt.% maleic anhydride from Shell, Netherlands
25	EXACT <sup>®</sup> 8201	ethylene-octene copolymer from DEX PLASTOMERS, Netherlands
	EXACT <sup>®</sup> MA	Maleic acid modified ethylene-octene copolymer, 0.9 wt.% MA
30		



### Examples and comparative experiments

The above-mentioned materials were used to produce the compositions listed in Table 1.

All compositions were obtained by premixing  
5 the components in the solid phase and subsequently feeding them to a twin-screw extruder and mixing them using a temperature profile of 150 to 260°C.

The properties of compositions 2, 4, 6, 8, 10, 11 and 13 were compared (compositions 6, 8, 10 according to the process of the invention, the other  
10 ones being comparative experiments).

#### Points examined:

- 1) The morphology, in particular the appearance and the particle size in the rubber phase. To  
15 this end TEM, transmission electron microscopy, pictures were made.
- 2) The mechanical behaviour, specifically the impact resistance (Izod, notched) and the creep behaviour on the basis of practical tests.

20 Morphology: The rubber phase in compositions 2, 4, 6, 8, 10 and 13 was dispersed in the polyamide matrix. Composition 11 had 2 rubber phases, viz. very fine Kraton particles < 100 nm and larger EXACT<sup>®</sup> particles, the diameter of which varied between  
25 0.5 and 2 µm. These particles were generally provided with a very thin shell of KRATON<sup>®</sup> FG. In composition 10 all KRATON<sup>®</sup> FG was present in the shell around the EXACT<sup>®</sup> particles, which were present in a particle size of about 0.1 - 0.6 µm.

30 In all cases in which a combination of functionalized rubber and a non-functionalized rubber was applied, the particles in the rubber phase were

observed to have a distinct sphere-shell structure.

Example 1 and comparative Experiment A

Bars with a diameter of 8 cm were extruded  
5 from composition 10 and composition 2. From these bars,  
hammer heads were machined, which were attached to a  
wooden stem by means of a pin. The hammer head obtained  
from composition 2 after some time exhibited play  
relative to the stem (comp. Exp. A), while the head  
10 from composition 10 (Example 1) was still firmly  
attached after 14 days of testing.

Example 2 and comparative Experiment B

From compositions 2, 4, 6, 8, 10 and 11  
15 plugs for attaching screws in brickwork were injection  
moulded. After the plugs had been placed in a series of  
uniform holes and screws had been inserted, the force  
needed to draw the plug with the screw out of the hole  
was measured after fixed intervals. The results are  
20 outlined in Table 1.

- does not meet the standard set
- o meets the standard set
- + more than meets the standard set

The plugs from compositions 2, 4 and 11  
25 (not according to the invention) are found to 'set'  
more rapidly, i.e. exhibit higher creep and can sooner  
be drawn out of the hole than the plugs from  
compositions 6, 8 and 10 according to the invention.

Table 1

Composition, parts by weight	1	2	3	4	5	6	7	8	9	10	11	12	13
AKULON® F 235C	100	75		90		90		90		90	95		90
AKULON® K 120			50		50		50		60			50	
AKULON® TP4	-	25											
EXXELOR®	-		50		20								
KRATON® FG	-								10		1		
C8-EXACT®	-						40		40		4		
C8-EXACT® MZA	-						10					50	
Composition 3				10									
Composition 5						10							
EPDM					30								
Composition 7								10					
Composition 9										10			
Composition 12													10
particle size [µm]	n.a.	0.4-2		0.5-4		0.5-3		0.4- 1.6		0.1- 0.6	0.3- 1.5		0.5- 3.0
IZOD notched 23°C [kJ/m²]	7.2	12.8	NB	12.5	NB	13.0	NB	13.5	NB	13.0	11.8	NB	12.4
creep		-		-		0		+		+	-		+

C L A I M S

1. Process for the preparation of an impact-resistant polymer composition comprising 0.5-75 parts by weight of a rubber composition (per 100 parts by weight of matrix polymer) by
  - a) melt mixing of matrix polymer A with a composition comprising the rubber composition dispersed in a matrix polymer B, with B optionally being A, and
  - b) the dispersion of said rubber composition in matrix polymer B having been obtained by melt mixing of matrix polymer B with a rubber composition that contains at least one functionalized rubber and at least one non-functionalized rubber.
2. Process according to claim 1, characterized in that the weight ratio of matrix polymer B to rubber composition lies between 80:20 and 30:70.
3. Process according to claim 1 or claim 2, characterized in that the rubber composition is a mixture of a functionalized and a non-functionalized rubber.
4. Process according to claim 3, characterized in that the functionalized rubber is present as a shell around a core of the non-functionalized rubber.
5. Process according to any one of the preceding claims, characterized in that the functionalized rubber is derived from a rubber that is different from the non-functionalized rubber.

6. Process according to any one of claims 3, 4 or 5, characterized in that the non-functionalized rubber is chosen from the group consisting of ethylene (C3-C20)  $\alpha$ -olefin copolymers.
- 5 7. Process according to claim 6, characterized in that the  $\alpha$ -olefin contains 6-20 carbon atoms and the ethylene- $\alpha$ -olefin copolymer is obtained by polymerization in the presence of a metallocene catalyst.
- 10 8. Process according to any one of claims 1-7, characterized in that matrix polymers A and B are chosen from the group consisting of polyamides, polyesters, polyacetals and polycarbonates.
9. Process according to claim 8, characterized in  
15 that the matrix polymers are chosen from the group of polyamides.
10. Process according to any one of claims 1-9, characterized in that the functionalized rubber is based on a styrene-butadiene tri-block copolymer.
- 20 11. Process according to any one of claims 1-10, characterized in that the functionalized rubbers are obtained by chemical modification by means of reaction with or by graft polymerization of the rubber with an unsaturated dicarboxylic acid  
25 anhydride, an unsaturated dicarboxylic acid or an unsaturated dicarboxylic acid ester.
12. Process according to any one of claims 1-11, characterized in that the rubber is not crosslinked.
- 30 13. Process according to any one of claims 1-12, characterized in that particles in which the

rubber composition in matrix polymer B is dispersed consist of a core of non-functionalized rubber and a shell of functionalized rubber.

14. Impact-resistant polymer composition obtained by  
5 the process according to any one of claims 1-13.
15. Object shaped from the melt of the polymer composition according to claim 14.
16. Granule mixture comprising the matrix polymer A and the polymer B in which a rubber composition is  
10 dispersed by meltmixing polymer B and the rubber composition that contains at least one functionalized rubber and at least one non-functionalized rubber.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 00/00352

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08J3/00 C08L77/00 C08L67/00 C08L69/00 C08L59/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
-Y	US 4 757 112 A (PHADKE SHRIKANT V) 12 July 1988 (1988-07-12) claims 1-19 ---	1-9, 11-15
Y	EP 0 878 510 A (MITSUI CHEMICALS INC) 18 November 1998 (1998-11-18) claims 1-8 ---	1-9, 11-15
A	EP 0 279 502 A (COPOLYMER RUBBER & CHEM CORP) 24 August 1988 (1988-08-24) claims 1-29 -----	1-6,8,9, 14,15

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

1 September 2000

Date of mailing of the international search report

12/09/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Decocker, L

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 00/00352

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4757112 A	12-07-1988	NONE	
EP 0878510 A	18-11-1998	CA 2237921 A JP 11029702 A SG 66461 A US 6008297 A	16-11-1998 02-02-1999 20-07-1999 28-12-1999
EP 0279502 A	24-08-1988	CA 1333431 A AU 606387 B AU 1195388 A DE 3879984 A DE 3879984 T JP 2659975 B JP 63254117 A US 5151466 A US 5244972 A	06-12-1994 07-02-1991 28-09-1989 13-05-1993 11-11-1993 30-09-1997 20-10-1988 29-09-1992 14-09-1993